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SUBSTRATE PROCESSING METHOD AND
SUBSTRATE PROCESSING APPARATUS

TRANSLATOR'S DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Ryoji Kosugi, declare and say:

that I am thoroughly conversant in both the Japanese and English languages;

that I am presently engaged as a translator in these languages;

that the attached document represents a true English translation of the above-identified Japanese application entitled "SUBSTRATE PROCESSING METHOD AND SUBSTRATE PROCESSING APPARATUS".

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 1st day of September, 2004.

Ryoji Kosugi
Translator

SUBSTRATE PROCESSING METHOD AND SUBSTRATE PROCESSING APPARATUS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a substrate processing method and a substrate processing apparatus, and more particularly to a substrate processing method and a substrate processing apparatus used for forming, on bottom surfaces and side surfaces or exposed surfaces of embedded interconnects which have been formed by embedding an electrical conductor (interconnect material) such as copper or silver into fine interconnect recesses provided in a surface of a substrate such as a semiconductor wafer, a conductive film having a function to prevent thermal diffusion of the interconnect material into an interlevel dielectric layer or a function to improve adhesiveness between the interconnects and an interlevel dielectric layer or a interlevel cap film (anti-oxidizing film), or a metal alloy film such as a magnetic film covering the interconnects by electroless plating.

Description of the Related Art

As a process for forming interconnects in a semiconductor device, the so-called "damascene process", which comprises embedding a metal (conductive material) into interconnect trenches and contact holes, is coming into practical use. This process includes embedding aluminum or, more recently a metal such as copper or silver in trenches

or contact holes, which have previously been formed in an interlevel dielectric layer, and then removing extra metal by chemical mechanical polishing (CMP) so as to flatten a surface of a substrate.

In a case of such interconnects, for example, copper interconnects, which use copper as an interconnect material, in order to improve the reliability, there has been employed a method in which a barrier film is formed on bottom surfaces and side surfaces of the interconnects to prevent thermal diffusion of the interconnects (copper) into an interlevel dielectric layer and to improve electromigration resistance of the interconnects, or a method in which an anti-oxidizing film is formed to prevent oxidation of the interconnects (copper) under an oxidizing atmosphere so as to produce a semiconductor device having a multi-level interconnect structure in which insulating films (oxide films) are subsequently laminated. Generally, metal such as tantalum, titanium, or tungsten, or nitride thereof has heretofore been used as this type of barrier film. Nitride or carbide of silicon has generally been used as an anti-oxidizing film.

As an alternative of the above methods, there has been studied a method in which bottom surfaces and side surfaces or exposed surfaces of embedded interconnects are selectively covered with a protective film made of a cobalt alloy, a nickel alloy, or the like to prevent thermal diffusion, electromigration, and oxidation of the interconnects. With regard to a non-volatile magnetic

memory, when memory cells are mounted with high density and a design rule is small, an electric density of copper interconnects increases causing the problem of electromigration. Furthermore, when a memory cell is small, a writing current increases during writing, and a crosstalk is a problem due to the approach of the cells. To solve this problem, it is considered that a yoke structure, in which portions around copper interconnects are covered with a magnetic film such as a cobalt alloy or a nickel alloy, is effective. The magnetic film is formed, for example, by electroless plating.

For example, as shown in FIG. 1, fine interconnect recesses 4 are formed in an insulating film (interlevel dielectric layer) 2 made of SiO_2 or the like, which has been deposited on a surface of a substrate W such as a semiconductor wafer. A barrier layer 6 of TaN or the like is formed on a surface of the insulating film 2, and a copper seed layer 7 is formed on the surface of the barrier layer 6, if necessary. Then, copper plating is carried out to deposit a copper film on the surface of the substrate W so as to embed copper in the recesses 4. Thereafter, CMP (chemical mechanical polishing) is carried out on the surface of the substrate W to flatten the surface of the substrate W, thereby forming interconnects 8 made of copper in the insulating film 2. A interconnect-protective film (cap material) 9 of a Co-W-P alloy film, which is obtained, for example, by electroless plating, is formed selectively

on surfaces of the interconnects (copper interconnects) 8 so as to protect the interconnects 8.

There will be described a process of forming a interconnect-protective film (cap material) 9 of a Co-W-P alloy film selectively on surfaces of interconnects 8 by using a conventional electroless plating method. First, the substrate W such as a semiconductor wafer, which has been carried out a CMP process, is immersed, for example, in dilute sulfuric acid or dilute hydrochloric acid having an ordinary temperature for about one minute to remove impurities such as a metal oxide film on a surface of an insulating film 2 and CMP residues such as of copper. After the surface of the substrate W is cleaned with a cleaning liquid such as pure water, the substrate W is immersed, for example, in a $PdCl_2/HCl$ mixed solution having an ordinary temperature for about one minute to adhere Pd as a catalyst to the surfaces of the interconnects 8 so as to activate exposed surfaces of the interconnects 8.

After the surface of the substrate W is cleaned (rinsed) with pure water or the like, the substrate W is immersed, for example, in a Co-W-P plating solution at 80°C for about 120 seconds to carry out electroless plating selectively on surfaces of the activated interconnects 8. Thereafter, the surface of the substrate W is cleaned with a cleaning liquid such as pure water. Thus, an interconnect-protective film 9 made of a Co-W-P alloy film is formed selectively on the exposed surfaces of the interconnects 8 so as to protect the interconnects 8.

SUMMARY OF THE INVENTION

When an interconnect-protective film (cap material) of a Co-W-P alloy film is formed by performing electroless plating, as described above, it is the general practice to perform a pre-cleaning (purifying) treatment for removing an oxide film on the interconnects, for example, and for removing CMP residues such as of copper remaining on an insulating film in order to prevent an alloy film from being formed on the insulating film, prior to a catalyst imparting treatment for imparting a catalyst such as Pd or the like to the surfaces of the interconnects. The pre-cleaning treatment generally carried out using a pre-cleaning liquid comprising an inorganic acid such as H_2SO_4 or HCl. The pre-cleaning liquid has etching power on copper. Therefore, at the same time that the pre-cleaning treatment is performed, part of the copper interconnect is damaged (etched), resulting in an increase in the resistance of interconnect.

When the pre-cleaning treatment is performed, copper of interconnects may slightly be dissolved. If the dissolved copper moves on an insulating film between the interconnects and is applied to the insulating film, the applied copper tends to provide a leakage current path. After the pre-cleaning treatment is performed, when the insulating film is rinsed with pure water after it is treated with the pre-cleaning chemical solution, if the insulating film is exposed to the chemical solution or the rinsing liquid for a long time, then the insulating capability of the insulating

film is lowered, possibly resulting in an increase in the leakage current. If the chemical solution remains on the surface of the substrate after it is treated with the chemical solution, then the within-wafer uniformity of the deposited film is adversely affected. Consequently, it is necessary to quickly remove the chemical solution remaining on the surface of the substrate.

From an apparatus viewpoint, on the other hand, if the above various processes are performed by respective dedicated units, then not only the number of processing tanks in the respective processes is increased, but also a limitation is imposed on efforts to shorten the time to transfer substrates with a transfer robot. As a result, not only the apparatus footprint is increased and the processing throughput is lowered, but also process control between the processes is complicated. In particular, if the substrate is left in an oxygen atmosphere for a long time between the catalyst applying treatment and the rinsing treatment or between the rinsing treatment and the plating process, then the surface state of the substrate is liable to change, and the electrical characteristics of the interconnects on the processed substrate are possibly adversely affected.

The present invention has been made in view of the above drawbacks. It is an object of the present invention to provide a substrate processing method and a substrate processing apparatus which are capable of lowering the initial cost and the running cost of the apparatus, do not require a wide installation space, do not degrade electrical

characteristics such as an interconnect resistance and a leakage current, and are capable of efficiently forming a high-quality alloy film on the surface of a metal region.

In order to achieve the above object, the present invention provides a substrate processing method comprising: preparing a substrate having a metal region on a surface thereof; performing a pre-plating treatment by bringing a pretreatment liquid into contact with the surface of the substrate to modify the entire surface thereof; removing the pretreatment liquid remaining on the surface of the substrate in a rinsing treatment; performing an electroless plating process on the surface of the substrate to selectively form an alloy film on the surface of said metal region; and post-cleaning the substrate after the electroless plating process and drying the substrate.

With the above arrangement, the processing time is greatly reduced. If the metal region is a metal interconnect such as a copper interconnect or the like, for example, then an increase in the interconnect resistance after the plating process is maximally reduced, a produced leakage current is minimized, and the alloy film can selectively be formed on the surface of the metal. Furthermore, the initial cost and running cost of the apparatus are held to a low level, and the processes can successively be performed without the need for a wide installation space.

The metal region comprises, for example, an exposed surface of an embedded interconnect formed in an insulator,

a metal film formed on the bottom and side surfaces of a recess for an embedded interconnect formed in the surface of an insulator, or an exposed surface of a metal interconnect formed in the surface of an insulator.

The pre-plating treatment preferably comprises a treatment of purifying the surface of the substrate and simultaneously imparting a catalyst to the metal region to activate the surface of the metal region.

By thus purifying the surface of the substrate and simultaneously imparting a catalyst to the metal region to activate the surface of the metal region in the pre-plating treatment which modifies the entire surface of the substrate, it is possible to prevent part of the metal region such as a copper interconnect or the like from being damaged (etched) or from being dissolved in the pretreatment liquid in the pre-plating treatment. The purification of the surface of the substrate removes a metal oxide film formed on the surface of the metal region, and impurities and impurity residues such as a metal or an organic substance on the surface of the substrate including the surface of the metal region.

While the pre-plating treatment is in progress, it is preferable to form a continuous pretreatment liquid on the surface of the substrate for thereby preventing the surface of the metal region which has been activated in the treatment from being re-oxidized due to direct exposure of the surface of the substrate to an external atmosphere.

The pretreatment liquid film may comprise a liquid film which is still with respect to the surface of the substrate or a liquid film which moves with respect to the surface of the substrate, produced when the substrate is treated while the surface of the substrate is facing upwardly. If the pretreatment liquid film comprises a liquid film which moves with respect to the surface of the substrate, then the pretreatment liquid film in the vicinity of the surface of the substrate can be updated at all times for increasing plating efficiency accompanied by the cleaning treatment and the catalyst imparting treatment.

It is preferable to keep the thickness of the pretreatment liquid equal to or lower than 10 mm for thereby consuming a small amount of pretreatment liquid required to treat one substrate. This is suitable for using the pretreatment liquid in a single-use batch (throwing away the pretreatment liquid after use).

The pre-plating treatment and the rinsing treatment are preferably performed by ejecting a chemical solution or pure water from a nozzle toward the surface of the substrate which faces downwardly.

By thus performing the pre-plating treatment and the rinsing treatment in such a spray-type application, the treatment liquid which is fresh at all times can be uniformly distributed and supplied to the surface of the substrate for a reduced processing time. The uniformity of the within-wafer processing can easily be improved by adjusting the position of the ejection point.

The time after the pre-plating treatment is completed until the rinsing treatment is started is preferably within 5 seconds, thereby minimizing a continued reaction due to the remaining liquid after the pre-plating treatment and oxidization of the activated metal surface.

The pre-plating treatment and the rinsing treatment are preferably performed while the substrate is being rotated.

By thus performing the pre-plating treatment and the rinsing treatment while the substrate is being rotated, the uniformity of the chemical solution reaction or cleaning on the entire surface of the substrate is increased. The substrate may be rotated at different rotational speeds in the pre-plating treatment and the rinsing treatment for thereby adjusting the reaction and cleaning efficiency or the within-wafer uniformity.

A nozzle used in the pre-plating treatment and a nozzle or nozzles used in the rinsing treatment are preferably connected to respective different flow path systems.

With this arrangement, the nozzle system used in the rinsing treatment is prevented from being contaminated by the pretreatment liquid, allowing the rinsing liquid to keep a stable cleaning ability.

The pre-plating treatment may be performed by immersing the substrate in the pretreatment liquid.

By immersing the substrate in the pretreatment liquid, the substrate is isolated from the external atmosphere while the substrate is being treated, preventing the surface of the activated metal region from being re-oxidized, and the

amount of dissolved oxygen in the pretreatment liquid can be adjusted to control the rate of a reaction such as in the catalyst imparting treating in the pre-plating treatment.

The substrate is preferably rotated at a high speed after the pre-plating treatment is completed.

The high-speed rotation of the substrate is effective to reduce the amount of the chemical solution which is carried away by the substrate and a jig that holds the substrate.

The pre-plating treatment is preferably performed using the pretreatment liquid which is prepared by mixing at least together catalytic metal ions and an acid having a function to purify the surface of the substrate.

It is thus possible in the pre-plating treatment to impart a catalyst to the surface of the metal region and simultaneously to remove an oxide film on the surface of the metal region and impurities such as metal residues or the like remaining on an interlevel dielectric layer, for example.

The rinsing treatment is preferably performed by cleaning the surface of the substrate with pure water or pure water having a reducing capability increased by electrolysis or dissolving a hydrogen gas.

It is thus possible to efficiently clean away the pretreatment liquid remaining on the substrate while preventing the metal region which serves as an interconnect or the like, for example, from being oxidized and also to prevent the acid pretreatment liquid from finding its way

into the plating solution to keep the plating solution stable.

The rinsing treatment may be performed by cleaning the surface of the substrate with an aqueous liquid prepared by mixing one component or some components of an electroless plating solution.

It is thus possible to efficiently clean away the pretreatment liquid remaining on the substrate while preventing the metal region which serves as an interconnect or the like, for example, from being oxidized.

The pre-plating treatment and the rinsing treatment are preferably performed in an atmosphere having less oxygen than the atmosphere.

It is thus possible to suppress the regeneration of an oxide film on the surface of the metal region to which the catalyst is imparted by the pre-plating treatment.

The electroless plating process is preferably performed in an atmosphere having less oxygen than the atmosphere.

It is thus possible to prevent the alloy film from being oxidized during its deposition for thereby forming an alloy film of stable film property.

The time interval after the pretreatment liquid remaining on the surface of the substrate is rinsed away until the electroless plating process is started should preferably be within 15 seconds, thereby minimizing re-oxidization of the surface of the metal region by the external environment after the pre-plating treatment.

At least one of a film thickness and a film property of the alloy film is preferably measured after the substrate is post-cleaned and dried.

By measuring the film thickness of the alloy film formed on the surface of the metal region and adjusting the processing time of the plating process on a next substrate, for example, depending on a change in the film thickness, the film thickness of the alloy film to be formed on the surface of the metal region can be controlled.

The compositions and component concentrations of the pretreatment liquid and a rinsing liquid therefore, and the temperature of the pretreatment liquid are preferably kept in predetermined ranges.

It is thus possible to impart a catalyst with stable nuclear density to the surface of the metal region to form an alloy film having stable film properties and uniform film thickness.

The concentration of an impurity mixed in the pretreatment liquid in the pre-plating treatment is preferably measured, and the impurity is preferably removed when the impurity reaches a predetermined concentration.

It is thus possible to prevent the function of the expensive pretreatment liquid from being lowered, and to use the pretreatment liquid stably over a long period.

The electroless plating process is preferably performed by keeping the temperature, composition, and component concentrations of a plating solution in predetermined

ranges, and controlling a plating process time with respect to a predetermined film thickness.

By thus controlling the plating time, a film thickness of the alloy film formed on the surface of the metal region can be adjusted.

The present invention also provides a substrate processing apparatus comprising: a pretreatment unit for performing a pre-plating treatment by bringing a surface of a substrate having a metal region into contact with a pretreatment liquid to modify the entire surface of the substrate, and a rinsing treatment for rinsing the pretreatment liquid remaining on the surface of the substrate after the pre-plating treatment; an electroless plating unit for performing an electroless plating process on the surface of the substrate after the pre-plating treatment to selectively form an alloy film on the surface of said metal region; and a post-treatment unit for post-cleaning the substrate after the electroless plating process and drying the substrate.

With the above arrangement, the overall apparatus is more compact, does not require a wide installation space, has a lower initial cost and a lower running cost, and can form an alloy film within a shorter processing time, than would be if the processing steps were performed by separate units (processing units). In particular, since waiting times or transfer times for the substrate between the processing steps can be adjusted to extremely short times,

it is possible to form a high-quality alloy film without causing its electrical characteristics from being degraded.

The pre-plating treatment may comprise a treatment of purifying the surface of the substrate and simultaneously imparting a catalyst to the metal region to activate the surface of the metal region.

The pretreatment unit preferably has a function to separate the pretreatment liquid used in the pre-plating treatment and a rinsing liquid used in the rinsing treatment from each other after the substrate is processed.

It is thus possible to perform the pre-plating treatment and the rinsing treatment successively within a single processing unit, and to individually retrieve the processing liquids (the pretreatment liquid and the rinsing liquid) for reuse. Furthermore, the time between the pre-plating treatment and the rinsing treatment on the substrate can be adjusted to an extremely short time.

The pretreatment unit preferably includes a liquid purifying device having a liquid purifying function to measure the concentration of an impurity mixed in the pretreatment liquid in the pre-plating treatment and to remove the impurity when the concentration of the impurity reaches a predetermined value.

It is thus possible to suppress contamination of the pretreatment liquid used in the pre-plating treatment and to enable the pretreatment liquid to have stable catalyzing power and cleaning power.

The substrate processing apparatus should preferably have a device for measuring at least one of a film thickness and a film property of the alloy film formed on the substrate dried by the post-processing unit.

It is thus possible to realize a highly reproducible deposited film.

Preferably, a plating condition is changed or the quality of the deposited film is determined based on a measured value from the device for measuring at least one of the film thickness and the film property.

At least one of the film thickness and the film property of the film formed on the exposed surface of the metal region is measure, and the processing time or the component concentrations of the plating solution in the plating process on a next substrate, for example, are adjusted depending on a change in the film thickness or the film property, for thereby controlling, with good reproducibility, the film thickness of the alloy film that is formed on the surface of the metal region.

The pretreatment unit and the electroless plating unit are preferably arranged to process the surface of the substrate which faces in the same orientation.

It is thus possible to process the substrate with the pretreatment unit and the electroless plating unit without inverting the substrate through 180° but keeping the surface of the substrate facing downwardly, for example, thus shortening the transfer time for the substrate and suppressing changes in the state of the substrate.

The pretreatment unit and the electroless plating unit preferably have a common substrate holding head.

It is thus possible to adjust the time interval after the pretreatment liquid is rinsed away until the plating process is started, to an extremely short time for forming an alloy film of stable film property. Furthermore, the number of times that the substrate is transferred by a transfer robot hand or the like is reduced to avoid undue contamination or damage of the reverse side of the substrate.

The substrate holding head is preferably arranged to seal simultaneously or selectively one of a peripheral portion of a face side of the substrate and a peripheral portion of a reverse side of the substrate.

By performing the pre-plating treatment with the pretreatment unit while sealing the peripheral portion of the face side of the substrate and also performing the rinsing treatment with the pretreatment unit and the plating process with the electroless plating unit while sealing the peripheral portion of the reverse side of the substrate, for example, it is possible to prevent an abnormal plated film from being produced on the peripheral portion of the substrate.

The pretreatment unit and the plating unit are preferably disposed in a housing having an opening defined in a portion thereof and a function to adjust an atmosphere therein independently of the apparatus in its entirety.

By transferring the substrate after it is rinsed by the pretreatment liquid to the plating unit in an atmosphere which contains less oxygen than the atmosphere, the substrate being processed is prevented from being exposed to an oxidizing atmosphere, and an alloy film of stable film property is obtained.

The substrate processing apparatus is preferably housed in a housing shielded against transmission of light from an external environment.

It is thus possible to eliminate the light-excited motion of electrons in devices, interconnects, etc. formed in a device surface of the substrate while the substrate is being processed, preventing damage from being made to the substrate devices.

According to the present invention, by successively performing processes for forming an alloy film selectively on the surface of the metal region on the surface of the substrate according to electroless plating, the overall apparatus is more compact, does not require a wide installation space, has a lower initial cost and a lower running cost, and can form an alloy film within a shorter processing time, than would be if the processing steps were performed by separate units (processing units). In particular, waiting times or transfer times for the substrate between the processing steps can be adjusted to extremely short times, or it is possible to form a high-quality alloy film while preventing its electrical characteristics from being lowered by successively

performing surface cleaning, catalyst imparting, rinsing, and plating processes in a hardly oxidizing atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view showing an interconnect-protective film formed by electroless plating;

FIG. 2 is a plan view showing the layout of a substrate processing apparatus according to an embodiment of the present invention;

FIG. 3 is a front view of a pretreatment unit at the time a substrate is transferred;

FIG. 4 is a front view of the pretreatment unit at the time a catalyst imparting treatment is performed;

FIG. 5 is a front view of the pretreatment unit at the time a purifying treatment is performed and a catalyst chemical solution is rinsed;

FIG. 6 is a systematic view of the pretreatment unit and an electroless plating unit;

FIG. 7 is an enlarged fragmentary cross-sectional view of a substrate holding head at the time a substrate is transferred;

FIG. 8 is an enlarged fragmentary cross-sectional view showing the manner in which a substrate receiver of the substrate holding head is lifted and a seal ring of a substrate guide is pressed against the lower surface of the peripheral edge of the substrate to hold the substrate;

FIG. 9 is an enlarged fragmentary cross-sectional view showing the manner in which the substrate is attracted while

the peripheral edge of the lower surface of the substrate on the substrate holding head is being sealed by the lower surface of an attracting ring, and the substrate is spaced from the substrate guide;

FIG. 10A is a schematic view showing the manner in which a substrate is pre-treated (in a purifying treatment and a catalyst imparting treatment), FIG. 10B is a schematic view showing the manner in which a chemical solution applied to the substrate is rinsed, FIG. 10C is a schematic view showing the manner in which the surface of the substrate is plated; and

FIG. 11 is a diagram showing a process flow of the substrate processing apparatus shown in FIG. 2.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

An embodiment of the present invention will be described below with reference to the drawings.

FIG. 2 is a plan view showing the layout of a substrate processing apparatus according to an embodiment of the present invention. As shown in FIG. 2, the substrate processing apparatus includes a loading/unloading unit 12 for placing and housing a substrate cassette 10 which houses therein substrates W (see FIG. 1) each having interconnects 8 made of copper or the like in interconnect recesses 4 that are defined in the surface of the substrate W. While the loading/unloading unit 12 shown in FIG. 2 houses one cassette 10 only, it may house a plurality of cassettes.

Within a rectangular housing 16 having an air discharge system, there are disposed a pretreatment unit 18 for simultaneously performing pretreatments on the substrate W prior to a plating process, e.g., a purifying treatment and a catalyst imparting treatment, using the same pretreatment liquid, an electroless plating unit 20 for performing an electroless plating process on the surface (to be processed) of the substrate W, a film thickness/film property measuring unit 22 for measuring at least one of a film thickness and a film property of a protective film (alloy film) 9 (see FIG. 1) which is formed on the surface of each of the interconnects 8 by the electroless plating process, and a post-cleaning unit (post-treatment unit) 24 for post-cleaning and drying the substrate W after it is plated. A first transfer robot 26 is disposed in a position sandwiched between the loading/unloading unit 12 and the film thickness/film property measuring unit 22, and a second transfer robot 28 is disposed in a position sandwiched between the pretreatment unit 18, the electroless plating unit 20, the film thickness/film property measuring unit 22, and the post-cleaning unit 24.

In this embodiment, a purifying treatment for purifying the surface of the substrate and a catalyst imparting treatment for imparting a catalyst to interconnects of metal are simultaneously performed as the pretreatments prior to the plating process, using the same pretreatment liquid. The pretreatments prior to the plating process may be treatments for bringing the surface of the substrate into

contact with a chemical solution to modify the entire surface of the substrate with the chemical solution, i.e., two different treatments for treating the surface of an insulating film 2 and the surfaces of the interconnects 8 as a metal region simultaneously with the same chemical solution in this embodiment.

A vertically movable and angularly movable turn shaft 30 is vertically mounted laterally of the pretreatment unit 18 and the electroless plating unit 20, and a swing arm 32 is fixed to the upper end of the turn shaft 30. The swing arm 32 has a free end with a downwardly oriented motor 34 mounted thereon. The motor 34 has an output shaft 36 having a lower end on which there is mounted a substrate holding head 38 for detachably holding the substrate W. The substrate holding head 38 faces downwardly. When the turn shaft 30 is turned about its own axis, the swing arm 32 swings horizontally, moving the substrate holding head 38 between a position directly above the pretreatment unit 18 and a position directly above the electroless plating unit 20. Therefore, the pretreatment unit 18 and the electroless plating unit 20 have the common substrate holding unit 38. The substrate holding unit 38 rotates when the motor 34 is driven.

As shown in FIG. 6, the pretreatment unit 18 and the electroless plating unit 20, and the turn shaft 30, the swing shaft 32, and the substrate holding head 38 are disposed in a housing 42 having an air supply/discharge system 40. The housing 42 can be closed and has its

atmosphere independently controllable when the substrate is processed.

The pretreatment unit 18 simultaneously performs pretreatments on the substrate W prior to a plating process, i.e., a purifying treatment for purifying the surfaces of the embedded interconnects 8 formed in the surface of the substrate W and the surface of the insulating film 2, and a catalyst imparting treatment for imparting a catalyst to the surfaces to be processed of the interconnects 8 to activate the surfaces after the purifying treatment. The pretreatment unit 18 also performs a rinsing treatment for rinsing away a pretreatment liquid (chemical solution) used to impart the catalyst, with a rinsing liquid. In this embodiment, these treatments are performed by the single pretreatment unit 18.

The pretreatment unit 18 is of the two-liquid separating type for preventing different liquids from being mixed with each other. As shown in FIGS. 3 through 5, the pretreatment unit 18 has an upwardly open processing tank 100 (see FIG. 6) having an inside diameter slightly greater than the outside diameter of the substrate holding head 38. The processing tank 100 has an inner tank 100a and an outer tank 100b. A pair of legs 104 attached to a lid 102 is rotatably supported on an outer circumferential surface of the inner tank 100a. A crank 106 is integrally coupled to each leg 104 and has a free end rotatably coupled to a rod 110 of a lid moving cylinder 108.

When the lid moving cylinders 108 are actuated, the lid 102 is moved between a processing position covering an upper end opening of the inner tank 100a and a retracted position laterally of the inner tank 100a. The lid 102 supports on its surface (upper surface) a nozzle plate 112 having a number of spray nozzles 112a for ejecting outwardly (upwardly) a rinsing liquid such as pure water, electrolyzed ion water having reducing power, or an aqueous liquid having one component or mixed components of an electroless plating solution.

As shown in FIG. 6, the processing tank 100 accommodates therein a nozzle plate 124 having a plurality of spray nozzles 124a for ejecting upwardly a pretreatment liquid which is supplied from a pretreatment liquid tank 120 upon actuation of a pretreatment liquid supply pump 122, the spray nozzles 124a being distributed uniformly over the entire transverse plane of the processing tank 100. A drainpipe 126 for discharging the pretreatment liquid (waste liquid) is connected to the inner tank 100a of the processing tank 100. The drainpipe 126 has a three-way valve 128 having an outlet port connected to a return pipe 130 for returning the pretreatment liquid (waste liquid) to the pretreatment liquid tank 120 for reuse when necessary.

The pretreatment liquid is prepared by mixing together catalytic metal ions and an acid having a purifying function to remove impurities including a metal oxide film on the surface of the metal region, or metal residues remaining on the surface of the metal region and the surface of the

insulating film on the substrate other than the metal region, or the like. By bringing the pretreatment liquid into contact with the surface of the substrate, a catalyst is imparted to the surfaces of interconnects, and simultaneously the oxide film on the interconnect metal is removed and the metal residues on the interlevel dielectric layer are removed. Specifically, the pretreatment liquid may comprise an aqueous liquid which is a mixture of at least one of palladium hydrochloric acid, palladium sulfuric acid, and palladium acetic acid and at least one of hydrochloric acid, sulfuric acid, fluoric acid, acetic acid, oxalic acid, formic acid, citric acid, and tartaric acid.

In this embodiment, the nozzle plate 112 mounted on the surface (upper surface) of the lid 102 is connected to a rinsing liquid supply source 132. The pretreatment liquid that remains on the surface of the substrate after the pretreatment is rinsed (cleaned) away using a rinsing liquid, e.g., pure water. A drainpipe 127 for discharging the rinsing liquid (waste liquid) is connected to the outer tank 100b of the processing tank 100.

Although pure water, for example, is used as the rinsing liquid to rinse away the pretreatment liquid in this embodiment, electrolyzed ion water having reducing power or reducing water ionized by a desired process may be used to efficiently rinse (clean) away the pretreatment liquid which remains on the substrate while preventing the interconnects from being oxidized. Furthermore, the pretreatment liquid may be rinsed away by cleaning the surface of the substrate

with an aqueous liquid comprising one component or mixed components of an electroless plating solution, thereby efficiently cleaning away the pretreatment liquid which remains on the substrate while preventing the interconnects from being oxidized.

The substrate holding head 38 which is holding the substrate W is lowered and positioned in the inner tank 100a of the processing tank 100, and then the spray nozzles 124a of the nozzle plate 124 disposed in the inner tank 100a ejects the pretreatment liquid to the substrate W. The pretreatment liquid can thus uniformly be ejected to the entire lower surface (to be processed) of the substrate W, and can be discharged from the drainpipe 126 while it is prevented from being scattered outwardly.

The substrate holding head 38 is lifted and the upper end opening of the inner tank 100a of the processing tank 100 is closed by the lid 102. The spray nozzles 112a of the nozzle plate 112 disposed on the upper surface of the lid 120 eject the rinsing liquid, such as pure water, electrolyzed ion water having reducing power, or an aqueous liquid having one component or mixed components of an electroless plating solution, to the substrate W held by the substrate holding head 38, thereby rising (cleaning) away the pretreatment liquid that remains on the surface of the substrate after the catalyst is imparted thereto. The rinsing liquid (waste liquid) after it has rinsed away the pretreatment liquid is collected into the outer tank 100b of the processing tank 100, and then discharged through the

drainpipe 127. In this manner, the rinsing liquid such as electrolyzed ion water having reducing power is prevented from flowing into the processing tank 100, so that two liquids will not be mixed with each other therein.

With the pretreatment unit 18, as shown in FIG. 3, while the substrate holding head 38 is lifted, the substrate W is inserted and held in the substrate holding head 38. Thereafter, as shown in FIG. 4, the substrate holding head 38 is lowered and positioned in the inner tank 100a of the processing tank 100 (see FIG. 6). The substrate holding head 38 is rotated to rotate the substrate W held thereby, and the spray nozzles 124a of the nozzle plate 124 disposed in the processing tank 100 ejects the pretreatment liquid to the substrate W, thereby applying the pretreatment liquid uniformly to the entire surface of the substrate W. The substrate holding head 38 is lifted and stopped at a predetermined position. As shown in FIG. 5, the lid 102 in the retracted position is moved to the position covering the upper end opening of the inner tank 100a of the processing tank 100.

Then, the spray nozzles 112a of the nozzle plate 112 disposed on the upper surface of the lid 120 eject the rinsing liquid, such as pure water, electrolyzed ion water having reducing power, or an aqueous liquid having one component or mixed components of an electroless plating solution, to the substrate W held and rotated by the substrate holding head 38. In this manner, the purifying treatment and the catalyst imparting treatment on the

substrate W using the pretreatment liquid, and the rinsing treatment using the rinsing liquid, such as pure water, electrolyzed ion water having reducing power, or an aqueous liquid having one component or mixed components of an electroless plating solution can be performed without mixing the two liquids with each other.

The pretreatment liquid tank 120 is associated with a pretreatment liquid purifying device 140 for measuring the concentration of impurities such as of copper or the like which have been mixed in the pretreatment liquid during the pre-plating treatment and removing the impurities when the concentration thereof reaches a predetermined value. The pretreatment liquid purifying device 140 is capable of preventing the pretreatment liquid to be used in the pre-plating treatment from being contaminated to allow the pretreatment liquid to have stable catalyzing power and cleaning power at all times. It is preferable to keep the temperature, composition, and component concentrations of the pretreatment liquid in predetermined ranges for imparting a catalyst with stable nuclear density to the interconnect surfaces to form an alloy film having stable film properties and uniform film thickness.

The lowered position of the substrate holding head 38 can be adjusted to adjust the distance between the substrate W held by the substrate holding head 38 and the nozzle plate 124 for adjusting, as desired, the area in which the pretreatment liquid ejected from the spray nozzles 124a of

the nozzle plate 124 and the ejected pressure of the pretreatment liquid.

The above embodiment uses one pretreatment liquid corresponding to the pre-plating treatment. If a plurality of types, i.e., two types, of pretreatment liquids are used in the pre-plating treatment, then the pretreatment unit may be associated with three independent systems which use three types of chemical solutions (including pure water). Specifically, a first system dedicated to a first pretreatment liquid, a second system dedicated to a second pretreatment liquid, and a third system dedicated to a rinsing liquid are connected to the same unit.

As shown in FIG. 6, the electroless plating unit 20 is associated with a plating tank 200 for storing therein a plating solution controlled at a predetermined temperature (e.g., 80°C). The plating tank 200 has a bottom connected to a plating solution supply pipe 208 extending from a plating solution supply tank 202 and having a plating solution supply pump 204 and a three-way valve 206. The plating tank 200 also has a plating solution retrieval groove 210 around its circumferential wall. In the plating process, the plating tank 200 is supplied with the plating solution from its bottom, and a plating solution overflowed from the plating tank 200 is retrieved from the plating solution retrieval groove 210 into the plating solution supply tank 202 for thereby circulating the plating solution.

A temperature sensor 214 for measuring the temperature of the plating solution introduced into the plating tank 200 and controlling a heater 216 and a flow meter 218 based on the measured temperature is disposed near the bottom of the plating tank 200.

In this embodiment, the electroless plating unit 20 also has a heating device 222 for using water which is heated by the heater 216 and passes through the flow meter 218 as a thermal medium, and indirectly heating the plating solution with a heat exchanger 220 disposed in the plating solution in the plating solution supply tank 202, and a stirring pump 224 for circulating and stirring the plating solution in the plating solution supply tank 202. This arrangement lends itself to a situation where the plating solution is used at a high temperature (about 80°C). This process is more effective to prevent unwanted substances from being mixed with the plating solution which is very delicate than the in-line heating process.

With the electroless plating unit 20, while the plating solution in the plating tank 200 is being circulated, the substrate W held by the substrate holding head 38 is rotated and lowered into the plating solution in the plating tank 200. At this time, a plating solution managing device 240 and the heating device 222 associated with the plating tank 200 keep the temperature of the plating solution, the composition of the plating solution, and the concentrations of the components of the plating solution in predetermined ranges. After the substrate W is immersed in the plating

solution for a predetermined time, the substrate W is pulled upwardly to a given position above the plating tank 200, and the substrate holding head 38 is stopped against rotation, whereupon the plating process is ended. By thus controlling the processing time, the film thickness of the alloy film formed on the surface of the base layer to be processed on the substrate is adjusted.

As shown in detail in FIGS. 7 through 9, the substrate holding head 38 has an attraction head 234 and a substrate receiver 236 surrounding the attraction head 234. The attraction head 234 and the substrate receiver 236 rotate in unison with each other through a splined structure upon energization of the motor 34, and are vertically movable relatively to each other upon actuation of a cylinder (not shown).

An attraction ring 250 having a lower sealing surface for attracting and holding the substrate W is mounted by a presser ring 251 to the peripheral edge of the lower surface of the attraction head 234. A recess 250a defined circumferentially continuously in the lower surface of the attraction ring 250 and a vacuum line 252 extending in the attraction head 234 communicate with each other through a communication hole 250b defined in the attraction ring 250. The recess 250a can thus be evacuated to attract and hold the substrate W. Since the substrate W is held under a vacuum created in a circumferential pattern having a small width (in the radial direction), any effect (flexure, etc.) that the vacuum has on the substrate W is minimized. The

substrate W can be released when N_2 and/or pure water is supplied to the vacuum line 252.

The substrate receiver 236 is of a downwardly open bottom cylindrical shape, and has a substrate insertion windows 236a defined in a circumferential wall thereof for inserting the substrate W therethrough into the substrate receiver 236, and a circular substrate guide 254 disposed on a lower end thereof and projecting inwardly. The substrate guide 254 has a seal ring 254a disposed on an inner circumferential end thereof and projecting slightly upwardly. Protrusions 256 each having a tapered surface 256a on its inner circumferential surface as a guide for the substrate W are disposed on the upper end of the substrate guide 254.

As shown in FIG. 7, with the substrate receiver 236 being lowered, the substrate W is inserted into the substrate receiver 236 through the substrate insertion window 236a. The substrate W is guided and positioned by the tapered surfaces 256a of the protrusions 256, and placed and held in a given position on the upper surface of the substrate guide 254. Then, the substrate receiver 236 and the attraction head 234 are displaced relatively closely to each other. As shown in FIG. 8, the upper surface of the substrate W placed and held on the substrate guide 254 of the substrate receiver 336 abuts against the attraction ring 250 of the attraction head 234. The substrate receiver 236 and the attraction head 234 are further displaced relatively closely to each other to press the seal ring 254a of the

substrate guide 254 against the lower surface of the peripheral edge of the substrate W. Thus, the substrate is held with the lower surface of the peripheral edge of the substrate W being sealed by the seal ring 254a.

For pre-treating the substrate W, for example, the recess 250a in the attraction ring 250 is evacuated through the vacuum line 252, as described above, to attract the substrate W while sealing the peripheral edge of the upper surface of the substrate W with the lower surface of the attraction ring 250. Then, the pretreatment liquid is ejected to the surface (lower surface) of the substrate W to pre-treat the substrate W for thereby preventing a catalyst from being imparted to the peripheral edge of the substrate W. For rinsing and plating the substrate W, as shown in FIG. 9, the substrate receiver 236 and the attraction head 234 are spaced from each other by a distance ranging from several mm to several tens mm, separating the substrate W from the substrate guide 254 and attracting and holding the substrate W only with the attraction ring 250. The peripheral edge of the surface (lower surface) of the substrate W is now purified by the rinsing liquid. Even if the peripheral edges of the face and reverse sides of the substrate are not sealed during the plating process, since no catalyst is applied to those peripheral edges, the peripheral edges of the substrate are not contaminated in the plating process.

In this embodiment, as shown in FIG. 10A, the seal ring 254a of the substrate guide 254 is pressed against the lower

surface of the peripheral edge of the substrate W to seal the lower surface of the peripheral edge of the substrate W with the seal ring 254a. Then, the spray nozzles 124a of the nozzle plate 145 eject the pretreatment liquid to the substrate W to perform pretreatments, i.e., a purifying treatment and a catalyst imparting treatment, on the substrate W.

As shown in FIG. 10B, the substrate W is attracted and held while sealing the peripheral edge of the upper surface of the substrate W with the lower surface of the attraction ring 250, and the substrate W is spaced from the substrate guide 254. Then, the spray nozzles 112a of the nozzle plate 112 eject the rinsing liquid, such as pure water, electrolyzed ion water having reducing power, or an aqueous liquid having one component or mixed components of an electroless plating solution, to the substrate W, thereby rising away the pretreatment liquid that is applied to the substrate W. At this time, the seal ring 254a of the substrate guide 254 and the outer peripheral portion of the surface of the substrate are cleaned by a rinsing liquid ejected from dedicated nozzles (not shown).

Furthermore, as shown in FIG. 10C, the substrate W is attracted and held while sealing the peripheral edge of the upper surface of the substrate W with the lower surface of the attraction ring 250, and the substrate W is spaced from the substrate guide 254. Then, the substrate W is immersed in the plating solution in the plating tank 200, so that the surface of the substrate is plated.

The time after the pre-plating treatment is completed until the rinsing treatment is started should preferably be within 5 seconds, thereby minimizing a continued reaction due to the remaining liquid after the pre-plating treatment and oxidization of the activated metal surface.

The time interval after the pretreatment liquid remaining on the surface of the substrate is rinsed away until the electroless plating process is started should preferably be within 15 seconds, thereby minimizing re-oxidization of the surface of the metal region by the external environment after the pre-plating treatment.

Although not shown in FIG. 6, the plating tank 200 may be of a double-walled structure which is substantially similar to the processing tank 100. If the plating tank 200 is of a double-walled structure, then the substrate can be transferred from the inner tank into the outer tank immediately after the plating process, and can immediately be subjected to a primary rinsing treatment. In this embodiment, the electroless plating unit 20 does not have a rinsing function. Immediately after the plating process, the substrate is transferred from the plating tank 200 to the pretreatment unit 18 and is subjected to a primary rinsing treatment in the outer tank 100b of the pretreatment unit 18.

The post-cleaning unit 24 serves to remove, in a secondary cleaning treatment, the plating solution remaining on the surface of the substrate W plated by the electroless plating unit 20 or an unwanted precipitated substance on the

insulating film, and also simultaneously to clean the reverse side of the substrate W. The post-cleaning unit 24 is also arranged to rotate the substrate W at a high speed to spin-dry the substrate W.

Specifically, the post-cleaning unit 24 has a substrate stage for detachably holding the substrate W with a clamp mechanism and rotating the substrate W at a high speed, and cleaning liquid supply nozzles for supplying a cleaning liquid such as pure water, a chemical solution, or the like to both the face and reverse sides of the substrate held by the substrate stage. While the substrate held by the substrate stage is being rotated, the face and reverse sides of the substrate are supplied with the cleaning liquid such as pure water, a chemical solution, or the like to remove the plating solution remaining on the surface of the substrate W or an unwanted precipitated substance on the insulating film and simultaneously to clean the reverse side of the substrate. Furthermore, the substrate W is rotated at a high speed by the substrate stage to spin-dry the substrate W which has been post-cleaned.

An electroless plating process performed by the substrate processing apparatus will be described below with reference to FIG. 11. In this embodiment, an electroless plating process for selectively forming alloy film (interconnect-protective film) 9 made of a Co-W-P alloy to protect the interconnects 8 as shown in FIG. 1 will be described below.

First, one substrate W is taken by the first transfer robot 26 out of the substrate cassette 10 placed on the loading/unloading unit 12 which stores substrates W each having interconnects 8 (see FIG. 1) on its surface, with their surfaces facing upwardly, and transferred to the film thickness/film property measuring unit 22. The substrate W placed on the film thickness/film property measuring unit 22 is received by the second transfer robot 28, which inverts the substrate W by 180° and transfers the substrate W to the substrate holding head 38. Specifically, as described above, with the substrate receiver 236 being lowered, the substrate W is inserted into the substrate receiver 236 through the substrate insertion window 236a. The substrate receiver 236 is lifted to press the seal ring 254a of the substrate guide 254 against the lower surface of the peripheral edge of the substrate W to hold the substrate W.

Then, the swing arm 32 is pivoted to move the substrate holding head 38 to the position directly above the pretreatment unit 18. The lid 102 is moved from the position covering the upper end opening of the processing tank 100 to the retracted position, and the substrate holding head 38 is lowered into a position in the inner tank 100a of the processing tank 100. The spray nozzles 124a of the nozzle plate 124 disposed in the inner tank 100a ejects the pretreatment liquid to the substrate W which has been held and rotated by the substrate holding head 38, thereby pre-treating the surfaces of the interconnects 8. For example, the pretreatment liquid has a liquid temperature of

25°C, and comprises a mixed solution of 0.005 g/L of $PdCl_2$ and 0.2 ml/L of HCl, or a mixed solution of 0.04 g/L of $PdSo_4$ and 20 ml/L of H_2SO_4.

In this manner, metal oxide film on the surfaces of the interconnects 8 is removed and CMP residues remaining on the surfaces of the interconnects 8 and the insulating film 2 are removed, and at the same time a catalyst of Pd is applied to the surfaces of the interconnects 8. That is, Pd nuclei as catalyst nuclei (seeds) are formed on the surfaces of the interconnects 8, activating the exposed surfaces of the interconnects 8. As described above, the pretreatment liquid purifying device 140 may be provided for measuring the concentration of impurities such as of copper or the like which have been mixed in the pretreatment liquid by the catalyst imparting treatment and removing the impurities when the concentration thereof reaches a predetermined value, so that the used pretreatment liquid may be circulated for reuse.

In the pre-plating treatment, the substrate W is preferably rotated for increasing the uniformity of a chemical solution reaction on the entire surface of the substrate W.

Then, the substrate holding head 38 is temporarily lifted, and, when necessary, the substrate W is rotated at a high speed to spin off the pretreatment liquid. Thereafter, as described above, the substrate W is attracted and held while sealing the peripheral edge of the upper surface of the substrate W with the lower surface of the attraction

ring 250, and then the substrate W is spaced from the substrate guide 254. Subsequently, the lid 102 is positioned in covering relation to the upper end opening of the processing tank 100, and the nozzles 112a of the nozzle plate 112 eject the rinsing liquid, such as pure water or electrolyzed ion water having reducing power, to the substrate W, thereby rinsing off the pretreatment liquid applied to the substrate.

In the rinsing treatment, the substrate W is preferably rotated to increase the uniformity of cleaning over the entire surface of the substrate.

While the substrate holding head 38 is holding the substrate W, the substrate holding head 38 is moved to a position directly above the electroless plating unit 20. With the plating solution being circulated in the plating tank 200, the electroless plating process is performed on the surface of the substrate W. Specifically, for example, the substrate W is immersed in a plating solution of Co-W-P at a liquid temperature of 80°C for 120 seconds, for example, to selectively perform the electroless plating process (electroless Co-W-P plating) on the surfaces of the activated interconnects 8. Thereafter, the substrate holding head 38 is lifted to perform the primary rinsing treatment after the plating process. In this manner, alloy film (interconnect-protective film) 9 made of a Co-W-P alloy are selectively formed on the surfaces of the interconnects 8 to protect the interconnects 8. The plating solution may have the following composition, for example:

Plating solution composition:

- $CoSO_4 \cdot 7H_2O$: 14 g/L
- $Na_3C_6H_5O_7 \cdot 2H_2O$: 70 g/L
- H_3BO_3 : 40 g/L
- $Na_2WO_4 \cdot 2H_2O$: 12g/L
- $NaH_2PO_2 \cdot H_2O$: 21 g/L
- pH : 9.5 (adjusted by NaOH)

The volume, the temperature, and the components of the plating solution are kept in predetermined ranges by the plating solution managing device 240.

It is preferable to fill or circulate an inactive gas or a reducing gas in the housing 42 to keep an atmosphere having less oxygen than the atmosphere in the housing 42, and to pre-treat, rinse, and plate the substrate in that atmosphere. In this manner, an oxide film is prevented from being regenerated on the surfaces of the interconnects 8 to which the catalyst has been imparted, and the protective film is prevented from being oxidized during film deposition, thus forming an alloy film of stable film properties.

The plated substrate is transferred from the substrate holding head 38 to the second transfer robot 28, inverted 180°, and then transferred to the post-cleaning unit 24. In the post-cleaning unit 24, while the substrate W is being held and rotated by the substrate stage, the cleaning liquid such as pure water or the like is supplied to the face and reverse sides of the substrate W to clean the face and reverse sides of the substrate W. The substrate stage

further rotates the substrate W at a high speed to spin-dry the substrate W after the post-cleaning treatment.

The spin-dried substrate W is then transferred by the second transfer robot 22 to the film thickness/film property measuring unit 22, which measures at least one of a film thickness and a film property of the alloy film 9 which is formed on the surface of each of the interconnects 8. After the film thickness or the film property is measured, the substrate W is returned by the first transfer robot 26 into the substrate cassette 10 placed on the loading/unloading unit 12.

The film thickness or the film property which is measured of the film formed on the exposed surface of each of the interconnects 8 is fed back before the electroless plating process is performed on a next substrate, and the processing time or the components of the plating solution in the plating process on the next substrate are adjusted depending on a change in the film thickness or the film property, for thereby controlling the film thickness or the film property of the alloy film that is formed on the surface of the base layer to be processed on the substrate.

In the present embodiment, a desired liquid such as pure water or the like can be used as the rinsing liquid for rinsing the pretreatment liquid that remains on the substrate after the pre-plating treatment.

In the above embodiment, the Co-W-P alloy film is used as an alloy film (interconnect-protective film) 9. However, an interconnect-protective film made of Co-P, Co-W-B, Co-B,

Ni-W-P, Ni-P, Ni-W- B, Ni-B, or the like may be used. While copper is used as the interconnect material in the above embodiment, a copper alloy, silver, a silver alloy, gold, a gold alloy, or the like may be used as the interconnect material.

In this embodiment, an alloy film is formed on the exposed surfaces of embedded interconnects formed in an insulator. An alloy film may be formed on the surface of a metal film formed on the bottom and sides of a recess for an embedded interconnect formed in the surface of an insulator, or an alloy film may be formed on the exposed surfaces, i.e., the upper and side surfaces, of a metal interconnect formed on the surface of an insulator.

The pre-plating treatment may be performed by immersing the substrate in the pretreatment liquid, as with the electroless plating process. According to such a process, the substrate is isolated from the external atmosphere while the substrate is being treated, preventing the surface of the activated metal region from being re-oxidized, and the amount of dissolved oxygen in the pretreatment liquid can be adjusted to control the rate of a reaction such as in the catalyst imparting treating in the pre-plating treatment.

What is claimed is:

1. A substrate processing method comprising:

preparing a substrate having a metal region on a surface thereof;

performing a pre-plating treatment by bringing a pretreatment liquid into contact with the surface of the substrate to modify the entire surface thereof;

removing the pretreatment liquid remaining on the surface of the substrate in a rinsing treatment;

performing an electroless plating process on the surface of the substrate to selectively form an alloy film on the surface of said metal region; and

post-cleaning the substrate after the electroless plating process and drying the substrate.

2. A substrate processing method according to claim 1, wherein said metal region comprises an exposed surface of an embedded interconnect formed in an insulator.

3. A substrate processing method according to claim 1, wherein said metal region comprises a metal film formed on the bottom and side surfaces of a recess for an embedded interconnect formed in the surface of an insulator.

4. A substrate processing method according to claim 1, wherein said metal region comprises an exposed surface of a metal interconnect formed in the surface of an insulator.

5. A substrate processing method according to claim 1, wherein said pre-plating treatment comprises a treatment of purifying the surface of the substrate and simultaneously imparting a catalyst to said metal region to activate the surface of the metal region.

6. A substrate processing method according to claim 1, wherein said pre-plating treatment and said rinsing treatment are performed by ejecting a chemical solution or pure water from a nozzle toward the surface of the substrate which faces downwardly.

7. A substrate processing method according to claim 6, wherein said pre-plating treatment and said rinsing treatment are performed while the substrate is being rotated.

8. A substrate processing method according to claim 6, wherein a nozzle used in said pre-plating treatment and a nozzle or nozzles used in said rinsing treatment are connected to respective different flow path systems.

9. A substrate processing method according to claim 1, wherein said pre-plating treatment is performed by immersing the substrate in the pretreatment liquid.

10. A substrate processing method according to claim 1, wherein the substrate is rotated at a higher speed after said pre-plating treatment is completed.

11. A substrate processing method according to claim 5, wherein said pre-plating treatment is performed using the pretreatment liquid which is prepared by mixing at least together catalytic metal ions and an acid having a function to purify the surface of the substrate.

12. A substrate processing method according to claim 1, wherein said rinsing treatment is performed by cleaning the surface of the substrate with pure water or pure water having a reducing capability increased by electrolysis or dissolving a hydrogen gas.

13. A substrate processing method according to claim 1, wherein said rinsing treatment is performed by cleaning the surface of the substrate with an aqueous liquid prepared by mixing one component or some components of an electroless plating solution.

14. A substrate processing method according to claim 1, wherein said pre-plating treatment and said rinsing treatment are performed in an atmosphere having less oxygen than the atmosphere.

15. A substrate processing method according to claim 1, wherein said electroless plating process is performed in an atmosphere having less oxygen than the atmosphere.

16. A substrate processing method according to claim 1, wherein at least one of a film thickness and a film property of said alloy film is measured after the substrate is post-cleaned and dried.

17. A substrate processing method according to claim 1, wherein the compositions and component concentrations of said pretreatment liquid and a rinsing liquid therefore, and the temperature of said pretreatment liquid are kept in predetermined ranges.

18. A substrate processing method according to claim 1, wherein the concentration of an impurity mixed in said pretreatment liquid in said pre-plating treatment is measured, and the impurity is removed when the impurity reaches a predetermined concentration.

19. A substrate processing method according to claim 1, wherein said electroless plating process is performed by keeping the temperature, composition, and component concentrations of a plating solution in predetermined ranges, and controlling a plating process time with respect to a predetermined film thickness.

20. A substrate processing apparatus comprising:

a pretreatment unit for performing a pre-plating treatment by bringing a surface of a substrate having a metal region into contact with a pretreatment liquid to modify the entire surface of the substrate, and a rinsing treatment for rinsing the pretreatment liquid remaining on the surface of the substrate after the pre-plating treatment;

an electroless plating unit for performing an electroless plating process on the surface of the substrate after the pre-plating treatment to selectively form an alloy film on the surface of said metal region; and

a post-treatment unit for post-cleaning the substrate after the electroless plating process and drying the substrate.

21. A substrate processing apparatus according to claim 20, wherein said pre-plating treatment comprises a treatment of purifying the surface of the substrate and simultaneously imparting a catalyst to said metal region to activate the surface of the metal region.

22. A substrate processing apparatus according to claim 20, wherein said pretreatment unit has a function to separate the pretreatment liquid used in said pre-plating treatment and a rinsing liquid used in said rinsing treatment from each other after the substrate is treated.

23. A substrate processing apparatus according to claim 20, wherein said pretreatment unit includes a liquid purifying device having a liquid purifying function to measure the concentration of an impurity mixed in said pretreatment liquid in said pre-plating treatment and to remove the impurity when the concentration of the impurity reaches a predetermined value.

24. A substrate processing apparatus according to claim 20, further comprising:

a device for measuring at least one of a film thickness and a film property of the alloy film formed on the substrate dried by said post-processing unit.

25. A substrate processing apparatus according to claim 24, wherein a plating condition is changed or the quality of the deposited film is determined based on a measured value from the device for measuring at least one of the film thickness and the film property.

26. A substrate processing apparatus according to claim 20, wherein said pretreatment unit and said electroless plating unit are arranged to process the surface of the substrate which faces in the same orientation.

27. A substrate processing apparatus according to claim 20, wherein said pretreatment unit and said electroless plating unit have a common substrate holding head.

28. A substrate processing apparatus according to claim 27, wherein said substrate holding head is arranged to seal simultaneously or selectively one of a peripheral portion of a face side of the substrate and a peripheral portion of a reverse side of the substrate.

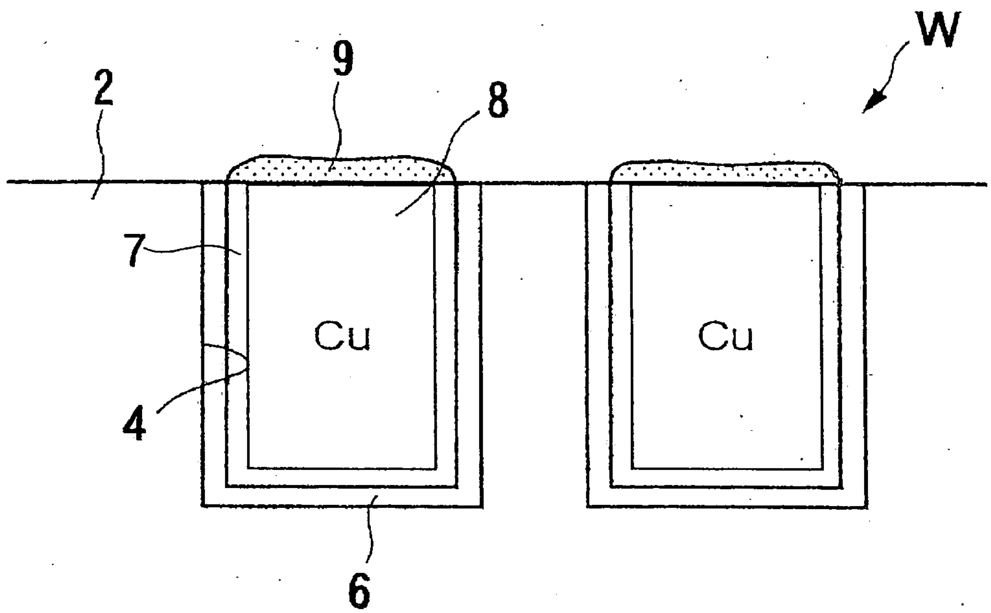
29. A substrate processing apparatus according to claim 20, wherein said pretreatment unit and said plating unit are disposed in a housing having an opening defined in a portion thereof and a function to adjust an atmosphere therein independently of the apparatus in its entirety.

30. A substrate processing apparatus according to claim 20, wherein the substrate processing apparatus is housed in a housing shielded against transmission of light from an external environment.

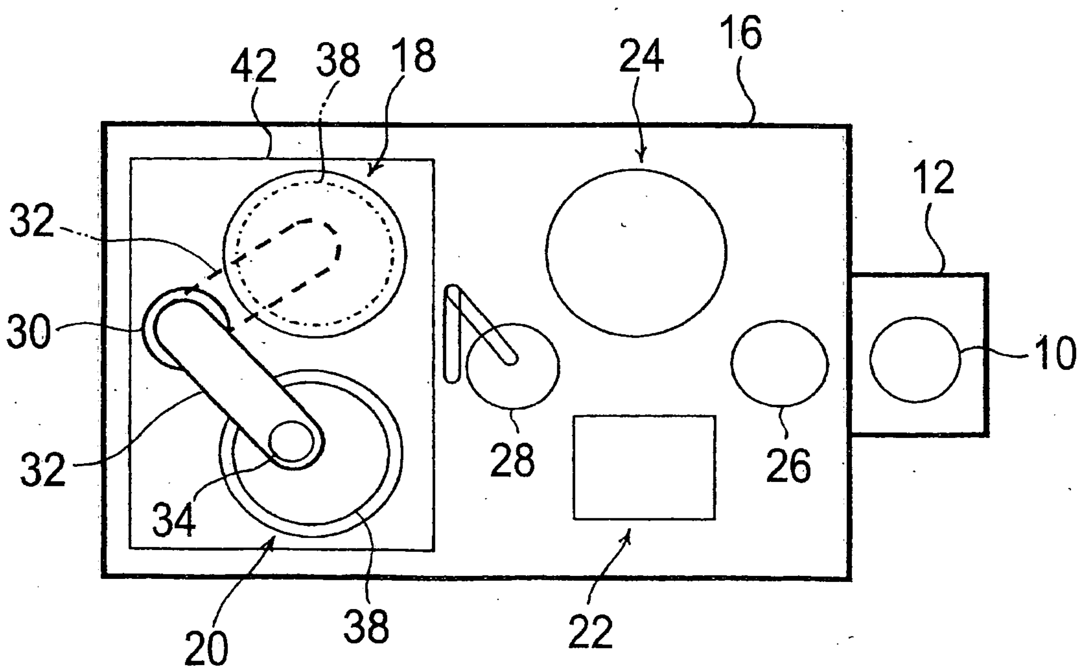
ABSTRACT OF THE DISCLOSURE

There is provided a substrate processing method which is capable of lowering the initial cost and the running cost of an apparatus, does not require a wide installation space, does not degrade electrical characteristics such as an interconnect resistance and a leakage current, and is capable of efficiently forming a high-quality alloy film on the surface of a metal region. The substrate processing method including: preparing a substrate having a metal region on a surface thereof, performing a pre-plating treatment by bringing a pretreatment liquid into contact with the surface of the substrate to modify the entire surface thereof, removing the pretreatment liquid remaining on the surface of the substrate in a rinsing treatment, performing an electroless plating process on the surface of the substrate to selectively form an alloy film on the surface of the metal region, and post-cleaning the substrate after the electroless plating process and drying the substrate.

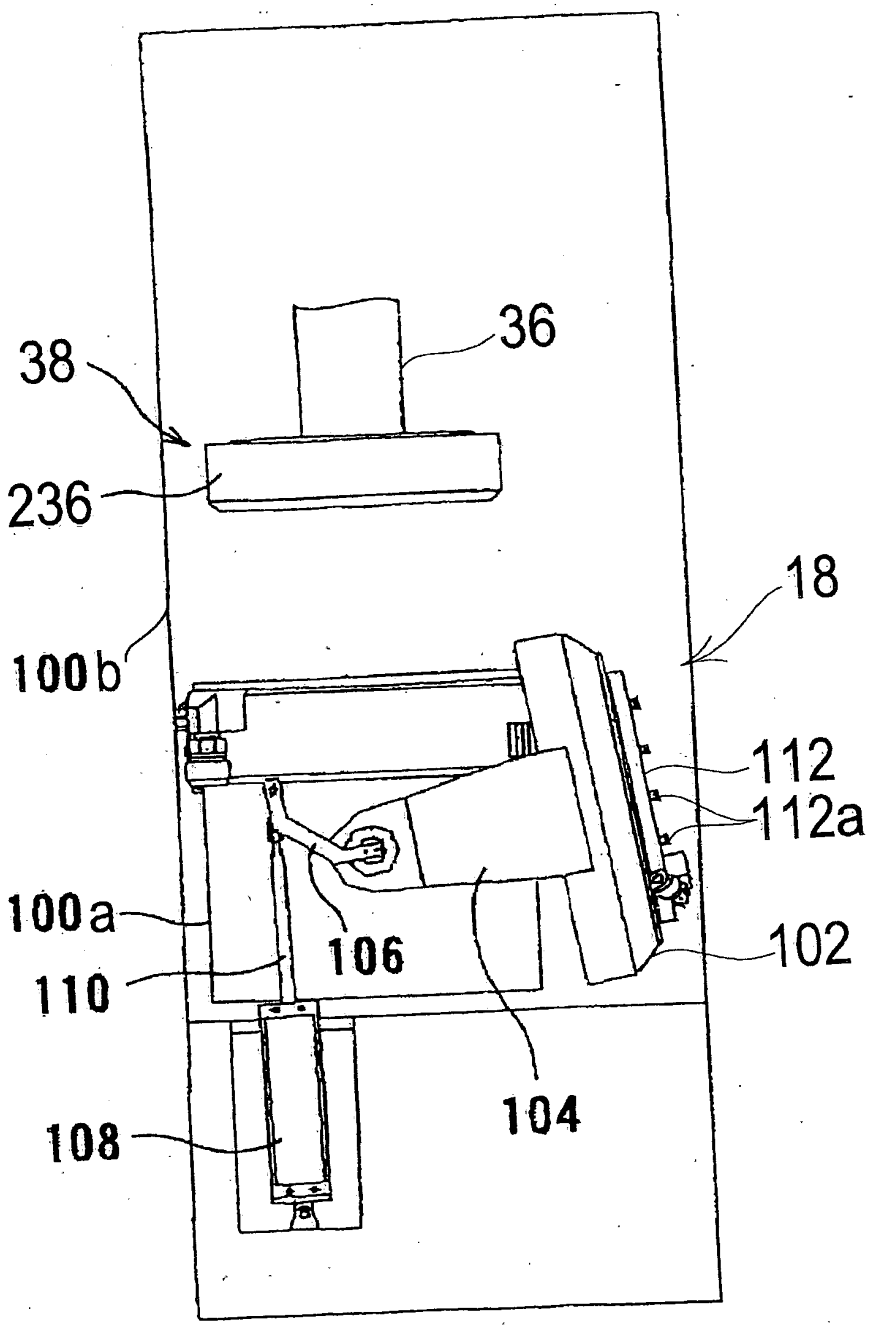
F I G. 1



F I G. 2



F I G. 3



F I G. 4

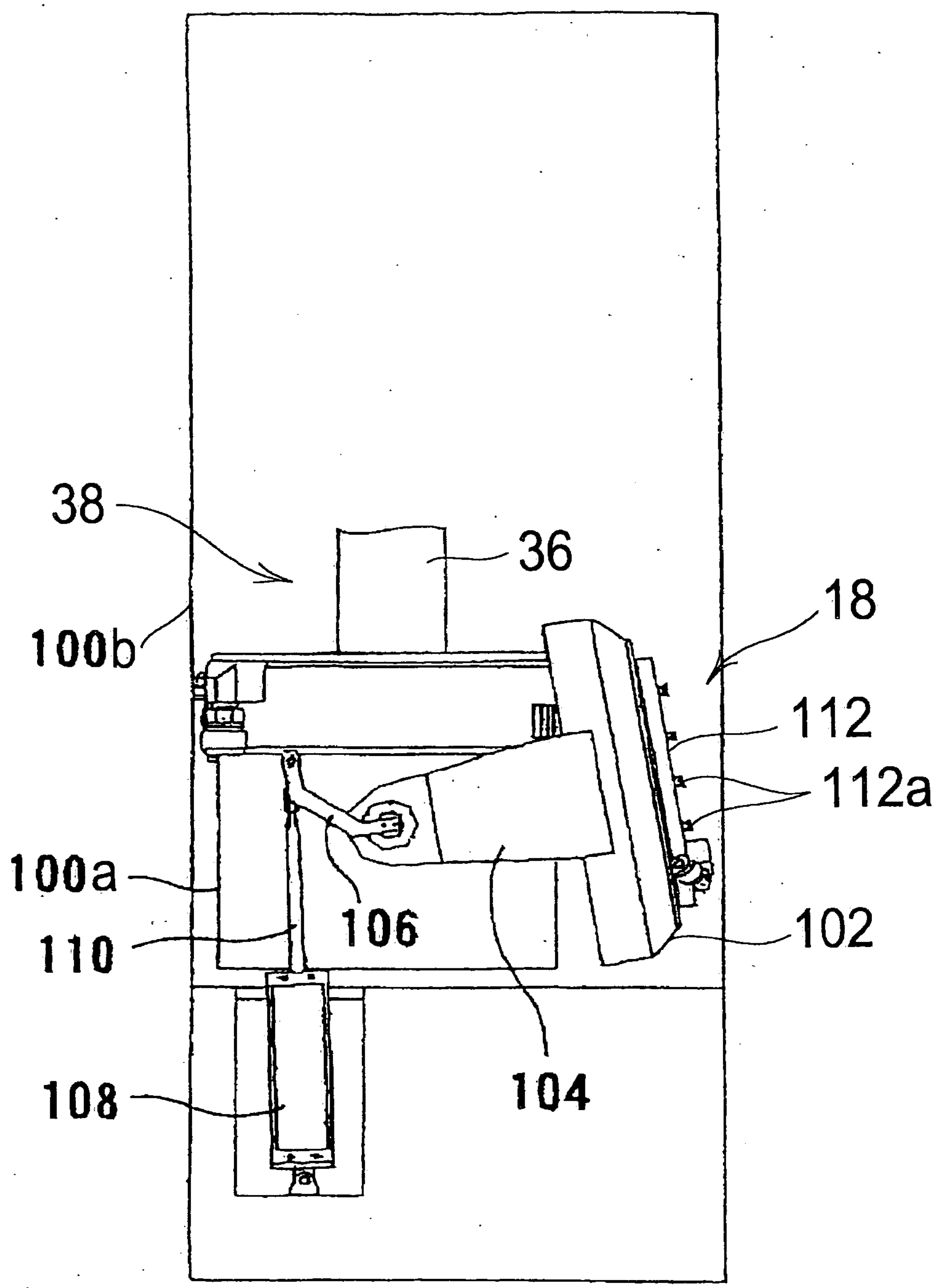
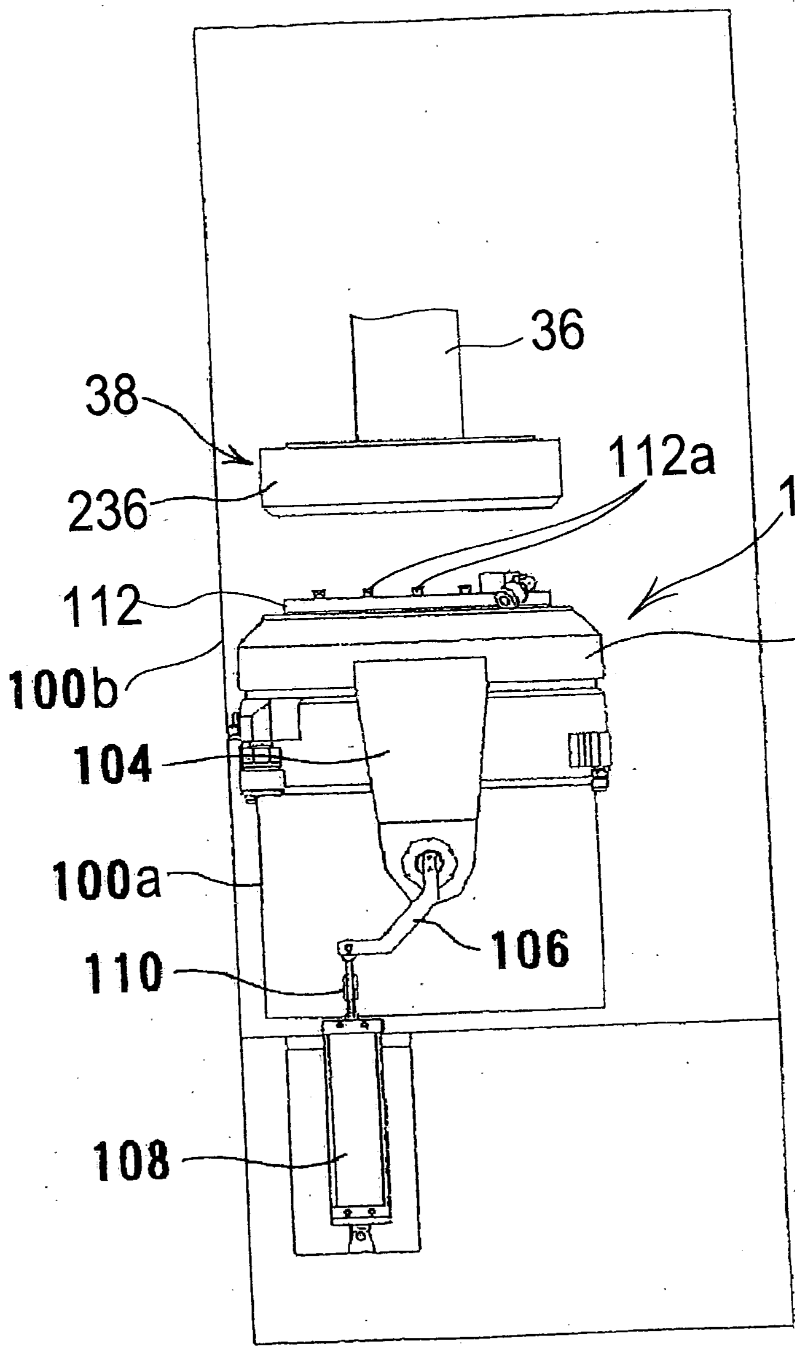
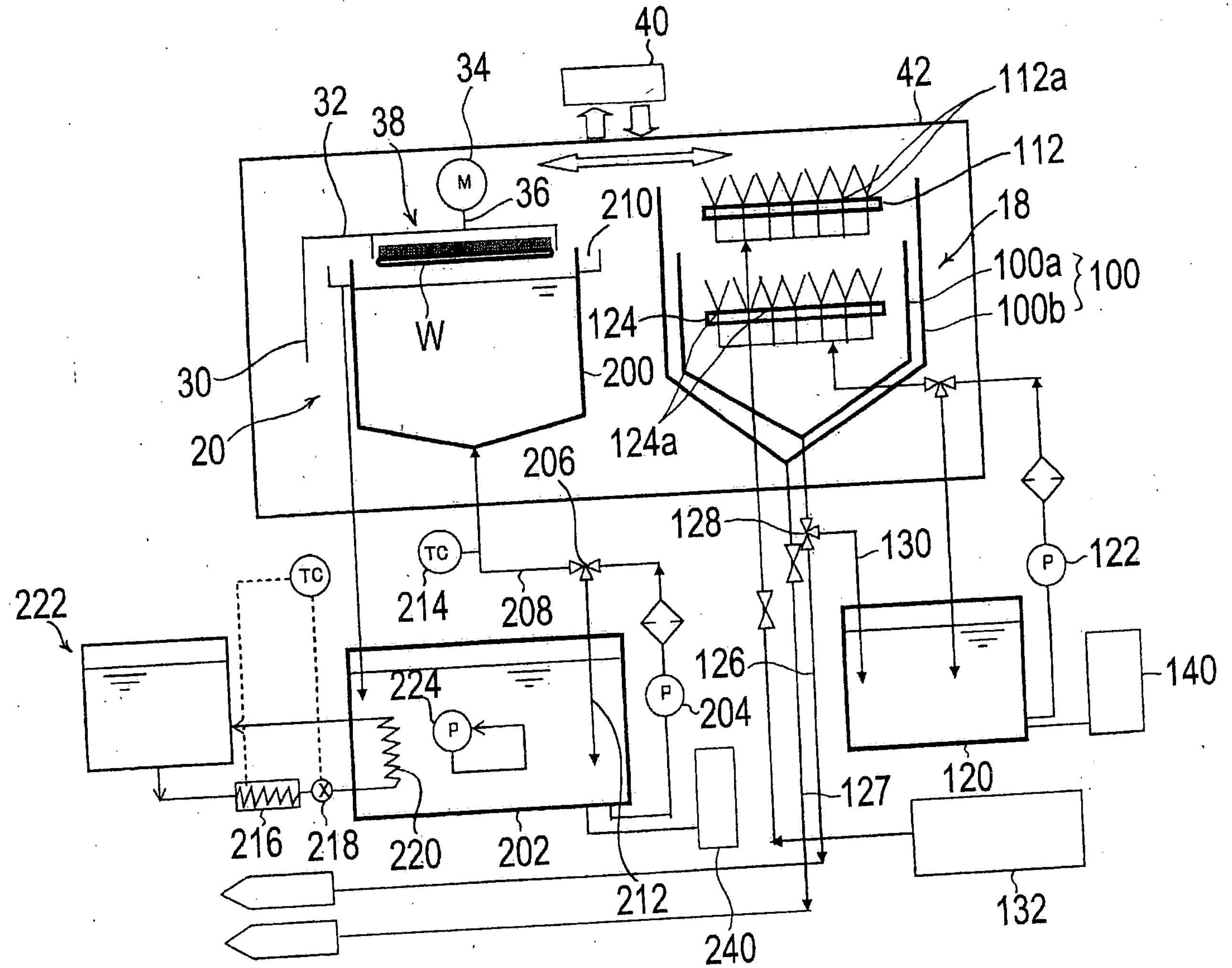


FIG. 5



F I G. 6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100b
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206
128
130
TC
214
208
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P
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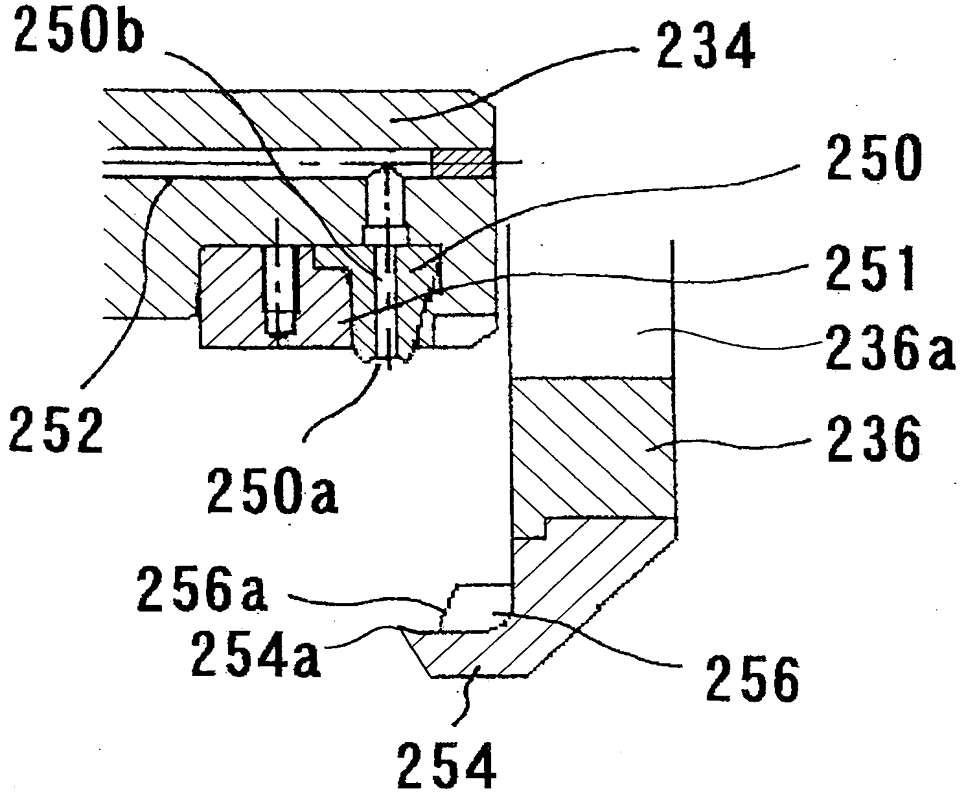
240
132

FIG. 7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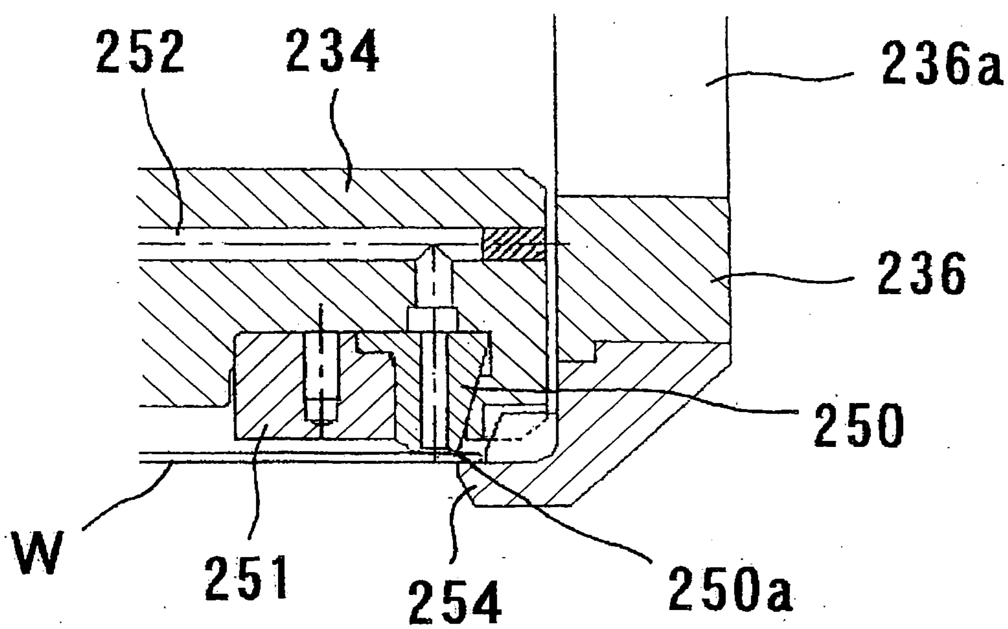
254a
256
254

FIG. 8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W
251
254
250a

F I G. 9

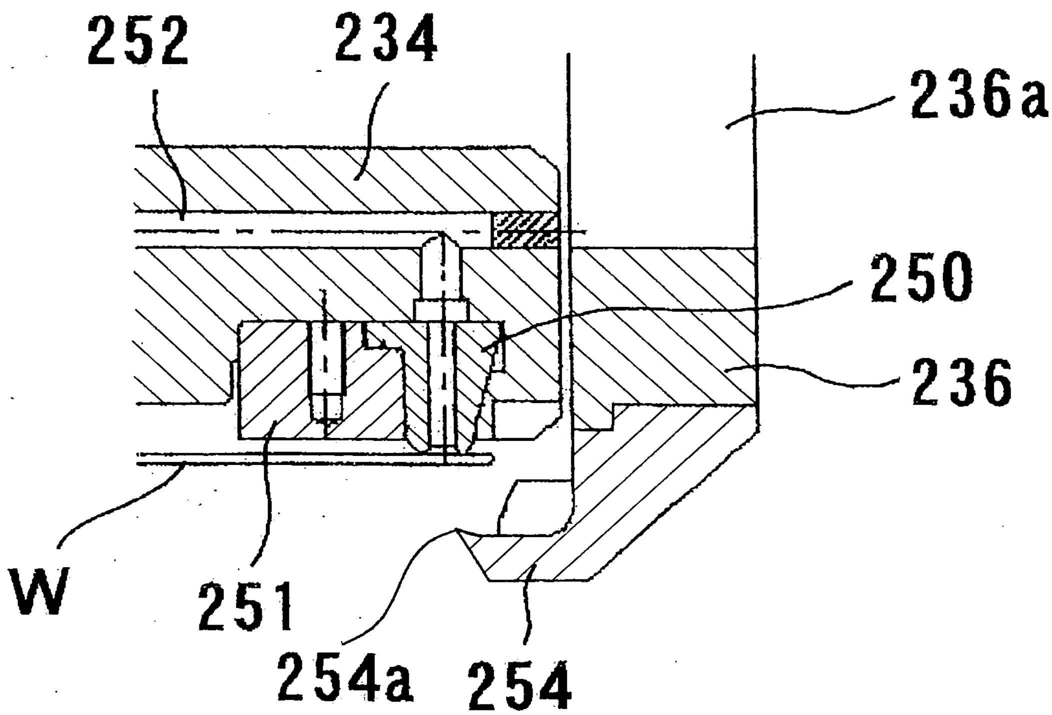


FIG. 10A

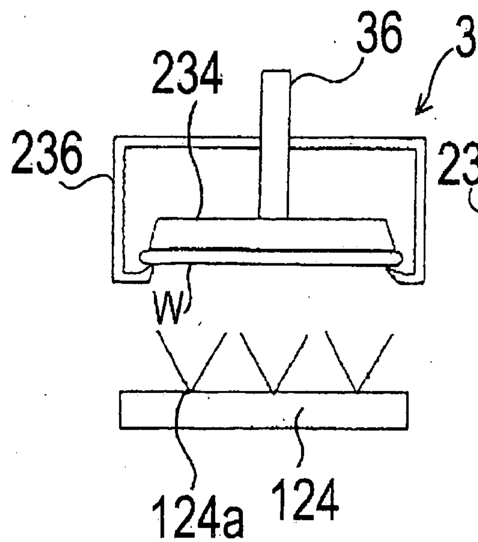


FIG. 10B

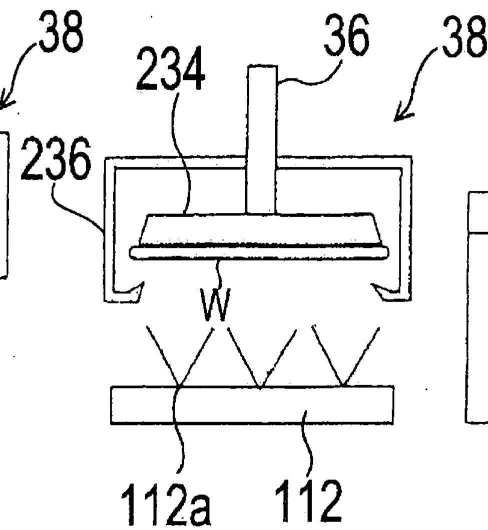


FIG. 10C

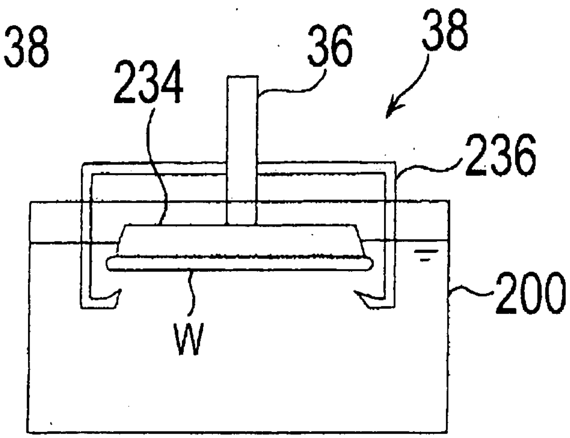
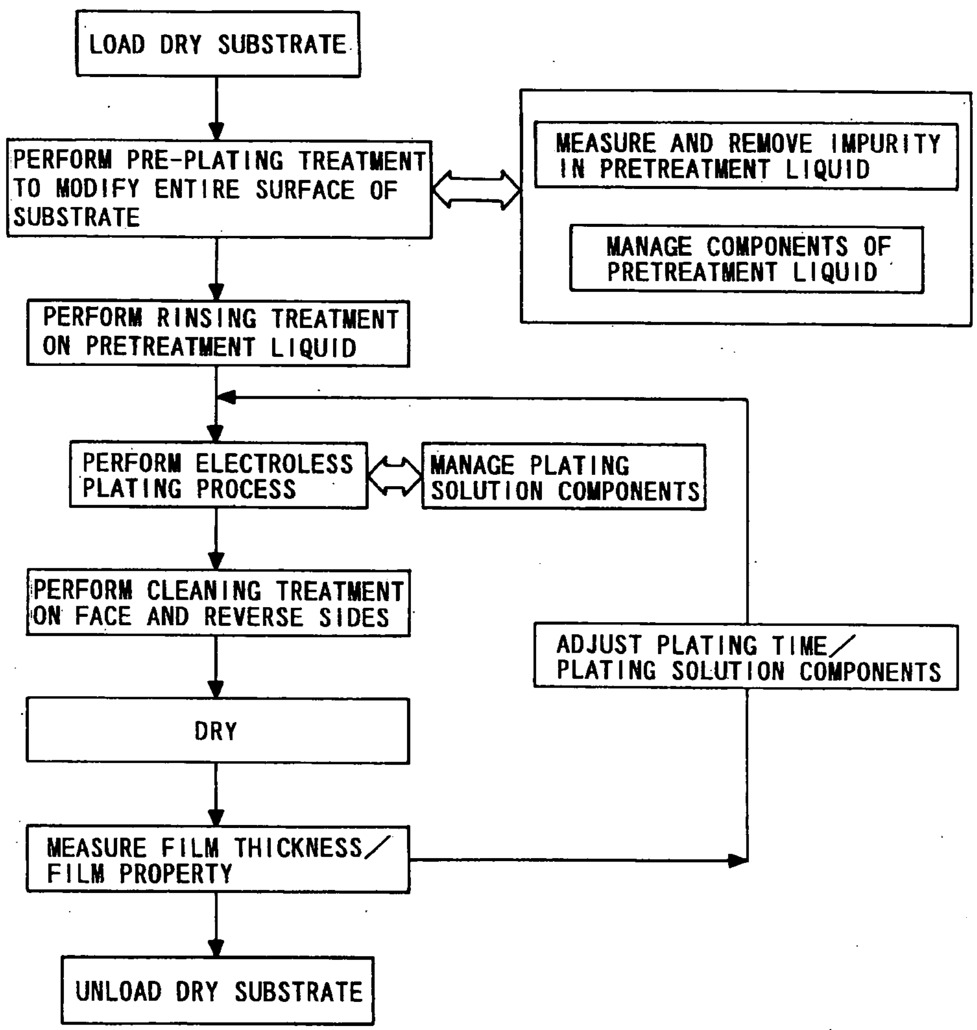


FIG. 11


LOAD DRY SUBSTRATE
PERFORM PRE-PLATING TREATMENT TO MODIFY ENTIRE SURFACE OF SUBSTRATE
MEASURE AND REMOVE IMPURITY IN PRETREATMENT LIQUID
MANAGE COMPONENTS OF PRETREATMENT LIQUID
PERFORM RINSING TREATMENT ON PRETREATMENT LIQUID
PERFORM ELECTROLESS PLATING PROCESS
MANAGE PLATING SOLUTION COMPONENTS
PERFORM CLEANING TREATMENT ON FACE AND REVERSE SIDES
ADJUST PLATING TIME/ PLATING SOLUTION COMPONENTS
DRY
MEASURE FILM THICKNESS/ FILM PROPERTY
UNLOAD DRY SUBSTRATE